SHEATH-PROTECTION MECHANISM AFFORDED BY CANLUB

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ABSTRACT

CANDU fuel elements can fail by stress corrosion cracking (SCC) of the Zircaloy-4 cladding during power ramps. Such failures result from the combined actions of stress concentrations and corrosive fission products. To combat the problem the CANLUB graphite coating was developed to reduce the operating stresses in the cladding below the critical level for SCC. However, it became evident that the observed beneficial effects of CANLUB coatings on fuel performance stemmed primarily from the interaction of the coating with fission products, rather than from lubrication of the fuel-claddinginterface. Therefore the coating must interact with corrosive species, either physically (as a barrier) or chemically. It was concluded, however, that the graphite coating is porous and ineffective as a barrier. Hence its effectivenessin preventing SCC must result from chemical interaction with the corrosive species.

Because of the interest in enhancing the reliability of CANDU reactors and in using enriched UO_2 *fuel, it is important to understand the chemistry of the interaction of the graphite in the CANLUB coating with fission products. It was first suggested by the authors that carbon could form compounds such as* $Zr_6I_{12}C$ *at reactor temperatures, and it was suggested that these compounds could immobilize corrosive iodine species (4). Unlike iodine and iodides,* Zr_xI_yC*-type compounds are relatively stable. Detecting* Zr_xI_yC *compounds in spent fuel bundles proved to be very difficult, but X-ray photoelectron spectroscopy (XPS) has shown that minute quantities of stable metal iodide(s) (probably* $CsZr_xI_yC$*-type compounds)were present on inter-pellet graphite discs from an irradiated fuel element. This was the first indication that fission-product iodine can be immobilized through its chemical interaction with CANLUB graphite. This paper gives an overview of the latest results on CANLUB development.*

1.0 INTRODUCTION

The CANLUB coating was originally developed to lubricate the fuel-cladding interface, reduce the operating stresses in the cladding, and so reduce the potential for stress corrosion cracking (SCC). It is now known that the lubricating effect is insufficient to account for the observed improvement in performance (1). Therefore, it is evident that CANLUB must also reduce the aggressiveness of potential corrodents. This reduction in corrosivity would be possible as a result of either the coating acting as a diffusional barrier, or by some chemical interaction between the coating and the corrodents.

The diffusional barrier scenario is now considered unlikely since post-irradiation examinations have shown that coatings are often not uniformly adherent following irradiation. Furthermore, diffusion coefficients for the relevant species are too large for the diffusion barrier concept to be a viable protection mechanism - even after irradiation, which appears to reduce the diffusion coefficient of I and Cs in graphite (2, 3).

Earlier studies at CRL suggested that the formation of carbon-iodine complexes was possible, but the structure of the compounds was unknown.

The possible roles of CANLUB graphite coatings on Zircaloy-4 in preventing fission-product-induced SCC at ~325°C have been reviewed recently (4). This review indicated possible mechanisms to explain the chemical attack of both the cladding and the protective oxide layer, and identified several mechanisms by which carbon could trap iodine. The most abundant iodine species in the fuel-cladding gap (as suggested by the review) is CsI, rather than I_2. CsI can react with ZrO_2 to yield ZrI_4 through the reaction:

$$4CsI + 3ZrO_2 \rightarrow 2Cs_2ZrO_3 + ZrI_4 \qquad (1)$$

Zirconium iodides are known to produce rapid stress-corrosion cracking of Zircaloy (5, 6). In order for a thin layer of graphite to minimize SCC, the graphite must interact chemically with the species causing the cracking, in this case ZrI_4. Several new zirconium-iodine compounds have recently been synthesized at 850°C (7). All of these compounds are structurally related to Zr_6I_{12} clusters. These cluster compounds are stabilized by common impurities such as B, Al, C, Si, Ge and P, because of the additional electrons contributed by the impurity atom. The following chemical equations summarize the formation of $(Cs)Zr_xI_yC$ from Zr, ZrI_4, CsI and CANLUB:

$$3Zr + 3ZrI_4 + C \rightarrow Zr_6I_{12}C \qquad (2)$$

$$5Zr + 7ZrI_4 + 2C \rightarrow 2Zr_6I_{14}C \qquad (3)$$

$$11Zr + 13ZrI_4 + 4C + 4CsI \rightarrow 4Cs(Zr_6I_{12}C)I_2 \qquad (4)$$

Experiments to identify the $Zr_6I_{12}C$ compound in irradiated fuel elements are critical for the determination of the fuel-sheath protection mechanism afforded by CANLUB. In the work reported here, selected samples of inter-pellet graphite discs from irradiated fuel elements (EXP-NPD-44) have been characterized by X-ray photoelectron spectroscopy (XPS). The chemical nature of iodine deposited on the irradiated graphite disc surface has been determined by correlating the Zr3d, I3d and C1s photoelectron binding energies (BEs) with those obtained from a well-characterized $Zr_6I_{12}C$ standard.

2.0 EXPERIMENTAL

2.1 Synthesis of $Zr_6I_{12}C$

Reactor-grade Zircaloy-4, DAG-154 (from Acheson Colliods of Brantford, Ontario) and reagent-grade ZrI_4 powder (from Alfa) were used. Both the Zircaloy-4 and ZrI_4 were used in the as-received condition, while the DAG-154 was passed through Zircaloy-4 tubing and then cured at 320°C for two hours in vacuum (10^{-3} torr) and cooled overnight in vacuum. These procedures were used to minimize the amount of moisture, organic solvents and entrapped gases in the graphite coating.

Because ZrI_4 is air- and moisture-sensitive, these compounds were handled in a dry box. Purified low-oxygen nitrogen served as an adequate working atmosphere. The nitrogen was passed over activated Linde Molecular Sieves to maintain an acceptably low moisture level.

All reactions were carried out in Zircaloy-4 tubes sealed by TIG (Tungsten Inert Gas) welding in helium or argon, or by R/MF (Resistance/Magnetic-Force) welding in high vacuum or carbon dioxide. Finally, the welded containers had to be placed in sealed quartz tubes under vacuum to protect them from attack by the ambient atmosphere at high temperatures, unless vacuum furnaces or noble-gas-filled furnaces were used.

The $Zr_6I_{12}C$ crystals were synthesized using 400 mg ZrI_4 and excess Zr (~10 g cladding) in an Ar-filled Zr-4 tube heated to 800°C over 14 days. Also, samples were reacted at 320°C for ~30 days with or without γ-irradiation in different environments. The test conditions are summarized in Table 1. Temperature was measured with thermocouples strapped to the outside of the quartz tubing.

TABLE 1: EXPERIMENTAL CONDITIONS FOR THE SYNTHESIS OF $ZR_6I_{12}C$

		CANLUB					
EXPERIMENT No.	FILLED GAS	CURED	UNCURED	NO CANLUB	γ-IRRADIATION	TEMP. °C	PERIOD (DAYS)
1	Ar	yes			no	800	14
2	Vacuum	yes			yes/no	320	30
3	He	yes			no	320	30
4	Ar	yes			yes/no	320	30
5	Ar		yes		no	320	30
6	Ar			X	no	320	30
7	CO_2			X	yes/no	320	30

For the γ-irradiation, the tubes were irradiated in an Ar-purged type 316L stainless steel autoclave. The autoclave was heated to 320 ± 2°C before being lowered into the Co-60 gammacell. The cumulative dose was calculated to be ~400 Mrad.

2.2 Surface Analysis of Inter-pellet Graphite Discs from Irradiated Fuel Elements

2.2.1 Sample Preparation

Due to difficulties previously encountered of trying to analyze the small amounts of powder scraped from the inside surface of the irradiated sheaths (DME-209 (8)), the inter-pellet graphite discs from an irradiated element, EXP-NPD-44 (9), were examined for crystallites of compounds. Inter-pellet graphite discs were the key to a separate program to reduce fuel operating temperatures. This element contained Aquadag ES242 sheath coating and 30 flat-end 1 pellets separated by 29 graphite discs. The element had been operated at 41 kW/m in the NPD reactor to a burnup of 98 MW.h/kgU and was then power-ramped in NRU to 74 kW/m with a final burnup of 107 MW.h/kgU.

All cutting operations were performed under argon cooling to avoid the decomposition of the compound by cooling water. The discs were removed by vibrating a piece of sectioned element. Those from the centre region of the element were analyzed.

2.2.2 Analytical Techniques

XPS: Surface composition and the chemical state of the samples were analyzed using a VG (Vacuum Generators) ESCALAB-II. Survey and high-resolution XPS spectra were recorded using a Mg X-ray source (1253.60 eV) operated at 12 kV and 20 mA emission current. The hemispherical analyzer was set to a pass energy of 20 eV in constant analyzer energy mode. The XPS spectra reported here were referenced to the graphite C1s peak at 284.6 eV.

SEM-EDX: Morphological observations were carried out using the JEOL JSM-840A scanning electron microscope. An accelerating voltage of 15 or 25 k and a probe current of about 10^{-10} A were used. Chemical composition data were obtained using a Tracor Northern (TN-5502) Energy Dispersive X-ray Spectrometer. A high-sensitivity semiconductor electron detector also enabled backscattered electron images to be obtained, which were useful for topographical and compositional observations.

XRD: The samples were examined in either a Debye-Scherrer powder camera or a Siemens horizontal diffractometer. The powder camera used filtered Co K_α radiation with a wavelength of 1.79 Å. The diffractometer used monochromated Cu K_α radiation with a wavelength of 1.54 Å. Both X-ray tubes were run at a power of about 1 kW. The powder camera specimens were mounted inside a quartz capillary (~0.1 mm ID) whereas the diffractometer specimens were fixed to a glass disc with an adhesive.

3.0 RESULTS AND DISCUSSION

3.1 Synthesis of $Zr_6I_{12}C$

The review (4) indicated that a possible mechanism for protection of the cladding is the formation of crystals of the stable compound (such as $Zr_6I_{12}C$). Reaction of ZrI_4 with CANLUB graphite-coated Zircaloy-4 cladding at 800°C produced well-facetted crystals up to ~50 μm in diameter on the CANLUB surface, as shown in the SEM micrographs, Figure 1a. These crystals were positively identified as $Zr_6I_{12}C$ by X-ray diffraction. Table 2 compares the stronger lines in the diffraction pattern with those obtained by Guthrie and Corbett [7].

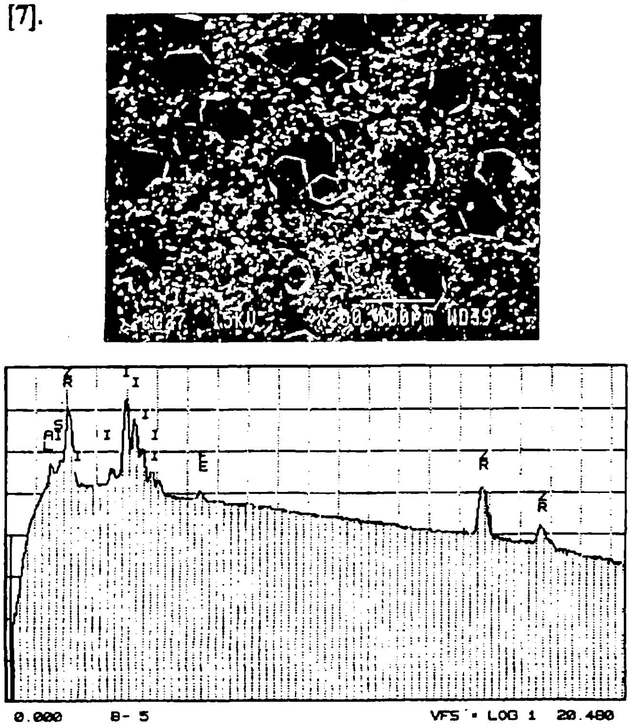


FIGURE 1: a) SEM MICROGRAPH, AND b) EDX SPECTRUM OF, $Zr_6I_{12}C$ PREPARED AT 800°C.

TABLE 2: STRONGER LINES IN THE X-RAY DIFFRACTION PATTERN ANALYSIS OF $ZR_6I_{12}C$ FROM THE LITERATURE AND FROM THE 800°C REACTION. INTENSITIES ARE GIVEN RELATIVE TO THE STRONGEST LINE AT 100%.

			LITERATURE			OBSERVED		
h	k	l	2θ	d-spacing Å	Intensity	2θ	d-spacing Å	Intensity
1	3	1	27.07	3.292	45	27.10	3.29	30
1	3	$\bar{2}$	31.25	2.860	100	31.25	2.86	100
1	3	4	44.54	2.032	32	44.60	2.03	50
5	2	0	45.01	2.012	32	45.10	2.01	45
1	3	$\bar{5}$	52.67	1.736	11	52.70	1.74	10
5	2	3	53.09	1.724	10	53.20	1.72	20
2	6	$\bar{1}$	53.32	1.717	10			
2	6	2	55.80	1.646	15	56.00	1.64	10
2	6	$\bar{4}$	65.16	1.430	11	65.25	1.43	16

The XPS survey spectra of the crystals indicated the presence of Zr, I, C, O, Sn, Fe and Cr, as shown in Figure 2. The binding energies (BE) of 619.8 eV for $I3d_{5/2}$, 182.7 eV for $Zr3d_{5/2}$ and 289.0 eV for C1s indicated the I-Zr-C bonds in the crystal (Figures 5a to 7a). An EDX analysis of the crystal (Figure 1b) also indicated the presence of Zr and I. Carbon X-rays cannot be detected because of their low energy: they are completely absorbed by the detector window (7.6 μm thick Be).

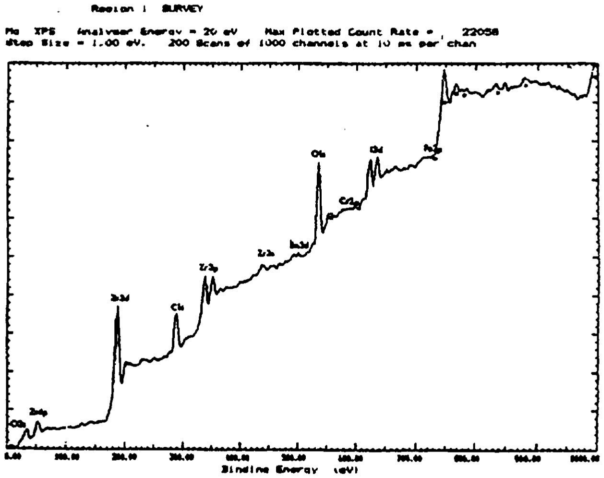


FIGURE 2: XPS SURVEY SPECTRUM OF $Zr_6I_{12}C$ PREPARED AT 800°C. "*" INDICATES AUGER PEAKS.

For the 320°C experiment, the Ar-filled and γ-irradiated sample exhibited a few isolated crystals, ~10 μm in diameter, having similar facets to those formed at 800°C, as shown in Figure 3a. XRD did not show the distinctive pattern of the cluster. However, EDX analysis of a crystallite showed approximately the same relative intensity of Zr and I (Figure 3b) as found with the $Zr_6I_{12}C$ crystals prepared at 800°C. Furthermore, γ-irradiated cladding samples without CANLUB but containing CO_2 showed a deposit giving Zr and I peaks in EDX analysis, again in the correct ratio for $Zr_6I_{12}C$. These deposits gave an XRD pattern showing α-Zr and smaller peaks where the two most prominent $Zr_6I_{12}C$ cluster peaks are expected, even though the deposit appearance was not like that of the 800°C crystals. In fact, crystals of some form could always be observed in all the experiments carried out at 320°C with the exception of experiment *#6* (Ar filling gas, no CANLUB).

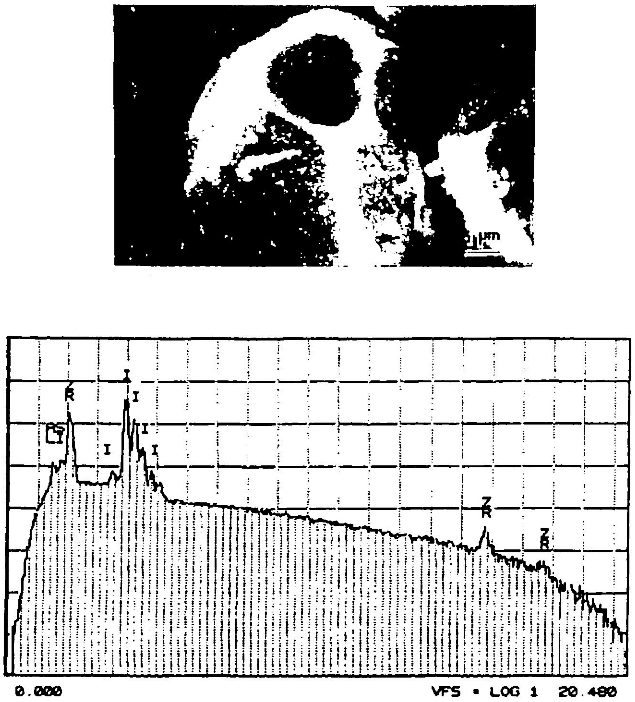


FIGURE 3: a) SEM MICROGRAPH AND b) EDX SPECTRUM OF, $Zr_6I_{12}C$ PREPARED AT 320°C WITH Ar As FILLING GAS AND γ-IRRADIATED.

Although the crystals did not give the distinctive XRD pattern and morphology of $Zr_6I_{12}C$ formed at 800°C, the correct relative EDX intensity ratio for Zr/I was observed. This ratio is important because it implies that the crystals have more or less the same composition as the clusters. The 800°C $Zr_6I_{12}C$ crystals were generally unreactive toward air at room temperature, but the 320°C crystals gradually decomposed to a greenish-black oily deposit on exposure to air. The above difference is probably associated with different degrees of perfection of the crystals, dependent at least in part on the rate of their growth.

In order to confirm the results and to provide confidence in the data, a calibration standard of $Zr_6I_{12}C$ was obtained from the AMES Laboratory, and this was used as a reference for XRD (Table 2), SEM (Figure 4a) and EDX (Figure 4b). From comparison of these spectra and micrographs with those obtained from the tests, it can be deduced that the crystals prepared at 320°C (at least those with CO_2) and 800°C had the correct properties.

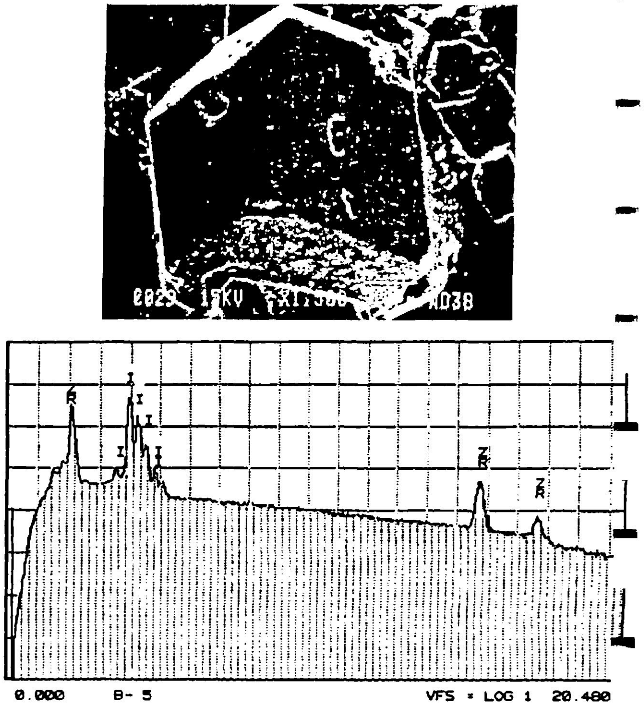


FIGURE 4: a) SEM MICROGRAPH, AND b) EDX SPECTRUM OF, $Zr_6I_{12}C$ OBTAINED FROM THE AMES LABORATORY.

3.2 Analysis of Irradiated Discs

In the present work the chemical nature of iodine trapped on the surface of inter-pellet discs from irradiated fuel has been determined by XPS to be metal iodide, probably a $CsZr_xI_yC$-type compound. Figures 5a, 6a and 7a show the XPS peaks for Zr, I and C respectively, from a $Zr_6I_{12}C$ standard. The BEs measured were: $Zr3d_{5/2}$-182.7 eV, $I3d_{5/2}$-619.8 eV, C1s-289.0 eV. Figures 5b and 6b show the small peaks obtained from the graphite discs at the $Zr3d_{5/2}$ and $I3d_{5/2}$ energies, respectively. Despite the low signal-to-noise ratio, there is evidence for peaks at the expected $Zr3d_{5/2}$ and $I3d_{5/2}$ BEs for $Zr_6I_{12}C$ (after expanding the intensity scale considerably).

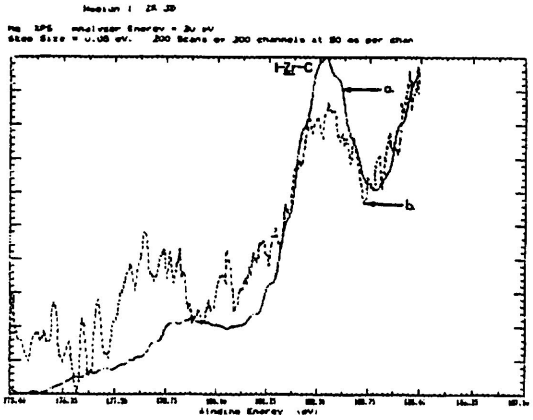


FIGURE 5: XPS $Zr3d_{5/2}$ SPECTRA OF: a) $Zr_6I_{12}C$ COMPOUND (MAX=2364 COUNTS), AND b) IRRADIATED GRAPHITE DISC (MAX=84 COUNTS).

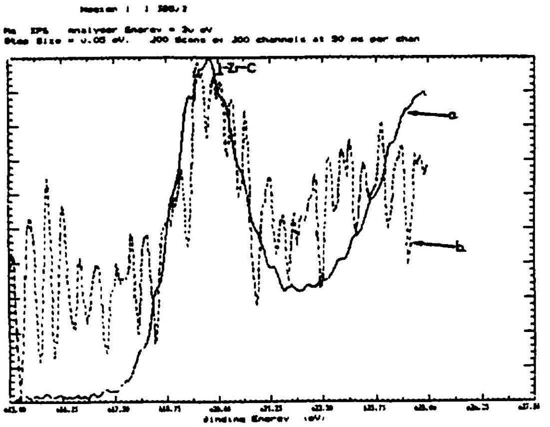


FIGURE 6: XPS $I3d_{5/2}$ SPECTRA OF: a) $Zr_6I_{12}C$ COMPOUND (MAX=2489 COUNTS), AND b) IRRADIATED GRAPHITE DISC (MAX=154 COUNTS).

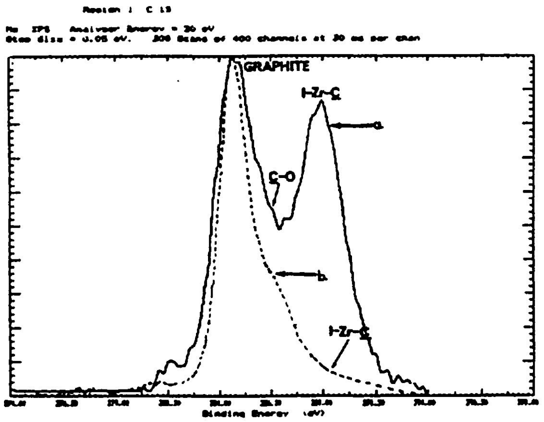
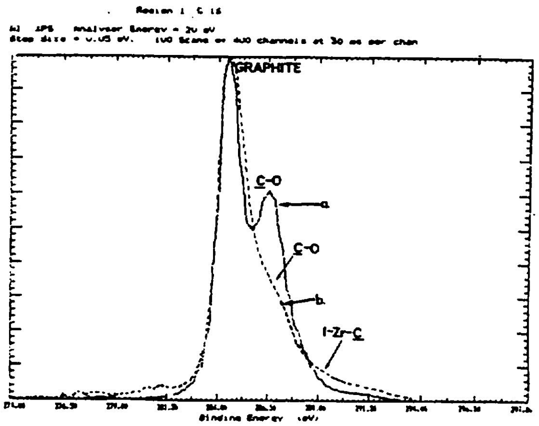
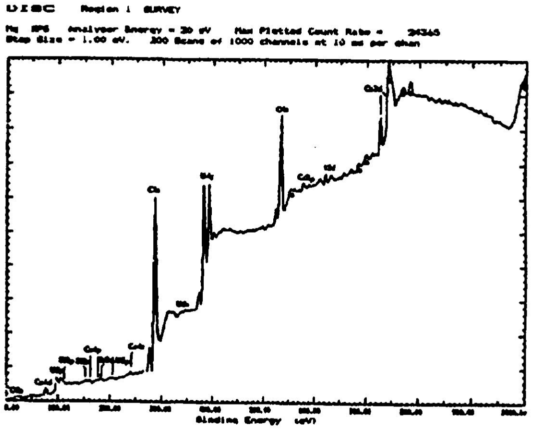


FIGURE 7: XPS C1s SPECTRA OF: a) $Zr_6I_{12}C$ COMPOUND, AND b) IRRADIATED GRAPHITE DISC.

For the C1s peak the situation is not so clear. The expected peak energy is 289.0 eV, but in the spectrum from the disc one observes a low intensity shoulder at this energy (Figure 7b). However, when the C1s spectra of the DAG-154 graphite and the disc are compared, as shown in Figure 8, a much longer tail or broader shoulder, on the high BE side of the disc, is seen. In fact, the C-O peak in the DAG-154 graphite is much stronger than in the disc, so the DAG-154 graphite should have a much stronger high energy shoulder, but this is not the case. Therefore, there must be one or more components present in the high BE tail. Possible candidates for such a high BE (289 eV and up) for carbon could be $-CO_3$, -C-F (10) or $Zr_6I_{12}C$. From the survey spectrum, shown in Figure 9, fluorine was not observed. Moreover, the presence of $-CO_3$ is unlikely because zirconium is a better getter of oxygen than C within a fuel element, and the fact that the CO peak in the irradiated disc is smaller than the DAG-154 graphite before irradiation suggests that graphite remains reduced under reactor conditions.



FIGURES 8: XPS C1s SPECTRA OF: a) DAG-154 GRAPHITE, AND b) IRRADIATED GRAPHITE DISC.



FIGURES 9: XPS SURVEY SPECTRUM OF THE IRRADIATED GRAPHITE DISC. "*" INDICATES AUGER PEAKS.

By using a peak-synthesis routine, the compound carbon peak at 289.0 eV can be deconvoluted. Figure 10 superimposes the original C1s spectrum on a synthesis of the three expected carbon peaks. The compound carbon peak is expected to have a low intensity because the total iodine inventory in a standard fuel element is only ~2.6 x 10^{19} atoms (i.e. 4 x 10^{-5} moles, or ~10 mg) and the photoelectron cross-section is much smaller for C than for Zr or I. Therefore, if the peaks for Zr and I in the disc are already of low intensity, the carbon peak must have a lower intensity still.

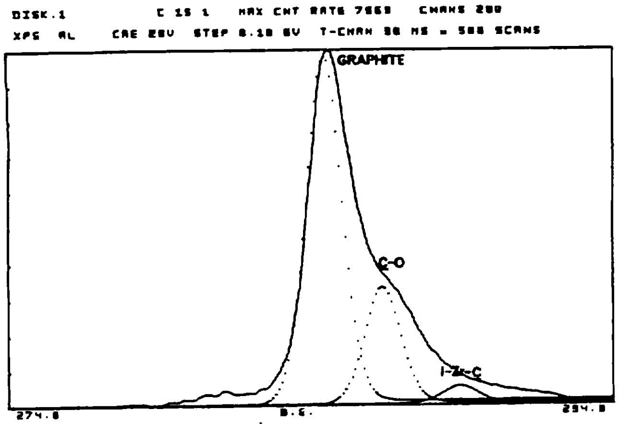


FIGURE 10: XPS C1s SPECTRUM OF THE IRRADIATED GRAPHITE DISC WITH PEAK-SYNTHESIZE ROUTINE.

XRD, SEM and EDX were also used to identify the $Zr_6I_{12}C$ compound on the irradiated discs. However, because of difficulties in crushing the discs finely enough to go into the capillary tube, only a small amount of material could be sampled before the tube was blocked. Therefore, XRD was able to indicate only the presence of graphite. The surface of the irradiated discs was clean except for small UO_x pieces sticking on the surface, and there was no evidence of $Zr_6I_{12}C$ crystals on the surface. Contamination of the surface by ZrO_2 as a result of cutting was not a problem, because particles of ZrO_2 were not observed on the SEM micrographs, and EDX microanalysis did not find any Zr signal. The EDX survey indicated only the presence of Si, Cl U, Ba, Fe, Ni and Cu; no evidence of Cs, I or Zr was noted.

XPS is surface-sensitive and can analyze the top 2-10 atom layers of a surface (~30 Å). XRD and EDX provide more of a bulk analysis, having a sampling depth of ~2-3 μm and ~1 μm, respectively. Therefore the observed difference in results from each of these techniques indicates that both the I and Zr are mostly trapped within the top few atom layers of the discs. This observation seems to be contradicted by the previous result that a thicker CANLUB coating offered better protection from SCC (11). However, the standard CANLUB coating certainly has different physical properties and porosity from those of the graphite discs. In order to clarify this issue, much higher burn-up elements (with graphite coating) have been examined, and the result will be reported in the "Third International Conference on CANDU Fuel".

The irradiated discs were examined by XPS without cooling by liquid nitrogen. Since many iodine compounds are either hygroscopic or deliquescent, and have high vapour pressures, the observed success in recording the XPS iodine spectrum without special sample transport or storage and cooling suggests that the iodide that was found in the graphite discs is stable. After leaving the discs exposed to ultra-high vacuum for five days at room temperature, the $Zr3d_{5/2}$ $I3d_{5/2}$ and C1s spectra remained unchanged, a further indication that the iodine deposits are not volatile or unstable under those conditions. ZrI_x compounds are not stable in air and no polymeric $(ZrI_2)_n$ surface structure was observed by SEM. The oxidation state of Zr on these surfaces is +4, and the observed peaks are definitely not due to ZrO_2 formed during cutting. There is some evidence that a carbon peak at 289.0 eV is present, and the BE of Zr and I in the discs is equal to those in the $Zr_6I_{12}C$ standard. Finally, iodine is stable or trapped on the surface along with Zr and C. Therefore, the compound that has been observed on the surface of the irradiated disc is a metal iodide; most probably a $Cs(Zr_xI_yC)$-type compound.

4. CONCLUSIONS

(i) Formation of the cluster compound $Zr_6I_{12}C$ has been achieved at 800°C and positively identified by X-ray diffraction. Also the cluster compound is believed to be formed at 320°C.

(ii) Some evidence has been found that CO_2 and γ-irradiation increase $Zr_6I_{12}C$ formation.

(iii) The observation that well-facetted crystals of $Zr_6I_{12}C$ were evenly distributed on the Zircaloy-4 tube surfaces suggests that $Zr_6I_{12}C$ cluster formation is a gas-phase reaction.

(iv) The chemical state of iodine deposited on the surface of inter-pellet graphite discs in an irradiated fuel element has been suggested by X-ray photoelectron spectroscopy to be a stable metal iodide, probably $Cs(Zr_xI_yC)$-type compound.

5.0 ACKNOWLEDGEMENTS

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